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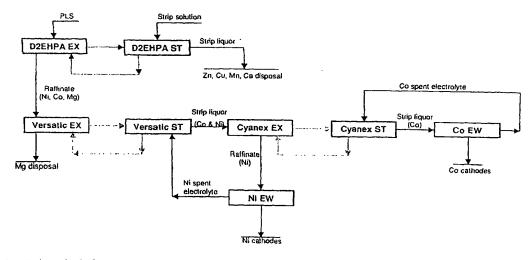
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(54) Title: SOLVENT EXTRACTION PROCESS FOR RECOVERING NICKEL AND COBALT FROM LEACH SOLUTIONS

(57) Abstract: A method of separating nickel, cobalt or both from other cations contained in a leach solution, the method including the steps of subjecting the leach solution to separate solvent extraction steps using an organophosphoric acid, a carboxylic acid and an organophosphinic acid.

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SOLVENT EXTRACTION PROCESS FOR RECOVERING NICKEL AND COBALT FROM LEACH SOLUTIONS

The present invention relates to a method of separating cobalt and nickel from other elements contained in an aqueous leach solution.

The world mineral industry is experiencing an unprecedented interest in nickel-cobalt extraction from laterite ores through high pressure acid leach (HPAL) and solvent extraction - electrowinning (SX-EW) processes. In WA, three nickel laterite projects have been commissioned. These are the Cawse project of Centaur Mining Ltd, the Bulong project of Preston Resources and the Murrin Murrin project of Anaconda Nickel Ltd. The HPAL process for the three projects is very similar, however the down stream processes (including SX) differ substantially.

In the Murrin Murrin process (Motteram et al., 1996), a sulfide precipitation is used to separate the nickel, cobalt, copper and zinc from impurities such as calcium, magnesium and manganese which remain in the leach solution. After solids/liquid separation, the nickel, cobalt, copper and zinc are re-leached under pressure with acid. Further solution purification is needed to separate nickel and cobalt from copper and zinc. The cobalt is then separated from nickel by solvent extraction with Cyanex 272. The nickel and cobalt are recovered by reduction with hydrogen. The drawbacks of the Murrin Murrin process are:

- The separation of manganese from cobalt by sulphide precipitation is incomplete and causes problems in the downstream processes,
- The leaching of sulphides needs high pressure and high temperature, indicating high capital and operating costs.
- The separation of other impurities such as copper and zinc from nickel and cobalt needs separate processes.

In the Cawse process (Manson et al., 1997), a
hydroxide precipitation is used to separate the impurities
such as calcium, magnesium and manganese (partly). After
5   solids/liquid separation, the nickel, cobalt, copper and
zinc are re-leached with an ammoniacal solution. Nickel and
copper are separated from cobalt and zinc by solvent
extraction with LIX84I. Further solution purification is
needed to separate nickel from copper and cobalt from zinc.
10   The nickel is recovered by electrowinning while cobalt is
precipitated as sulphide. The drawbacks of the Cawse
process are:
   • The use of ammoniacal leaching to separate manganese
     from cobalt results in complexity of the flowsheet and
15   causes serious problems in the downstream processes,
   • The reductive stripping of cobalt from organic
     extractant and the re-oximation of the organic
     extractant cause organic degradation (Kindred, 2000),
     which in turn results in crud formation,
20   • Ammonia is expensive and the scrubbing and recovery of
     ammonia are difficult,
   • Cobalt product containing zinc is a semi-product,
     indicating revenue loss.

25   The Bulong process (Taylor and Cairns, 1997),
uses a direct solvent extraction approach. Cobalt, copper,
zinc and manganese are separated from nickel, calcium and
magnesium by solvent extraction with Cyanex 272. The nickel
in the raffinate is separated from calcium and magnesium by
30   solvent extraction with Versatic 10 and then electrowon.
The solution containing cobalt, copper, zinc and manganese
is subjected to sulphide precipitation, solids/liquid
separation and acid pressure re-leach to separate cobalt,
copper and zinc from manganese. The copper is eliminated
35   from the solution by ion exchange and zinc by solvent
extraction with D2EHPA. The cobalt is then recovered from
the purified solution by electrowinning. The drawbacks of

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the Bulong process are:

- Manganese is separated from cobalt by sulphide precipitation and other impurities are separated by different further processes (ion exchange and further SX),

- Gypsum precipitation occurs in both Cyanex 272 and Versatic 10 circuits,

- Aqueous feed solution with its original volume is treated twice - in both the Cyanex and Versatic 10 SX circuits. This requires larger circuits (higher capital expenditure) than if the valuable metal (nickel) were concentrated by extraction into the organic phase in the first circuit.

        Currently used processes all incorporate precipitation and re-leach steps. Bulong and Murrin Murrin employ sulfide precipitation and acid re-leach, whereas Cawse employs hydoxide precipitation and ammoniacal re-leach. These steps require additional chemical reagents, precipitation, separation and leaching equipment, and additional operating costs.

        Recovery of nickel and cobalt from purified leach solutions by electrowinning, precipitation or any other appropriate process, is best performed after the metals have been concentrated to an appropriate level (often of the order of 50g/L). In laterite leach solutions, typical nickel and cobalt concentrations may be 1.0 - 4.0 g/L nickel and 0.1 -0.4 g/L cobalt.

        An object of the present invention is to provide processes for separating cobalt and nickel from impurities contained in leach solutions that concentrate the nickel and cobalt to levels appropriate for recovery by electrowinning, precipitation or any other appropriate process.

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According to the present invention there are provided methods of separating nickel, cobalt or both from other cations contained in a leach solution, the method including the steps of subjecting the leach solution to separate solvent extraction steps using an organophosphoric acid, a carboxylic acid and an organophosphinic acid.

In a preferred embodiment of the invention, the carboxylic acid extraction step is conducted with a mixture of carboxylic acid and a synergist that is capable of increasing the pH gap, ΔpH_{50}, between isotherms for nickel and cobalt and those for manganese and calcium. However, the use of the synergist is not always required. Whether or not a synergist is used will depend on the ordering of the three solvent extraction steps, and the cations present on the liquor being subjected to the octacarboxylic acid solvent extraction.

The pH_{50} value is the pH at which 50% metal extraction is achieved. Thus, ΔpH_{50} is the difference between the pH_{50} values for two metals.

In another embodiment of the present invention, there is provided a method for separating nickel, cobalt or both from other cations contained in a leach solution, the method involving subjecting the leach solution to separate solvent extraction steps using:
(a)   an organophosphinic acid; and
(b)   a carboxylic acid in combination with a synergist that is capable of increasing the pH gap, ΔpH_{50}, between isotherms for nickel and cobalt and those for manganese and calcium.

In the most preferred embodiment of the invention, the carboxylic acid is 2-hexyl, 2-methyl octacarboxylic acid or a carboxylic acid having extraction characteristics similar to or the same as 2-hexyl, 2-methyl

octacarboxylic acid. The term carboxylic acid is used in
its broadest sense to refer to any organic carboxylic acid.
Carboxylic acids have the formula RCOOH, in which R
represents any optionally substituted aliphatic or aromatic

5   group, or combinations of these groups, including
optionally substituted alkyl, alkenyl, alkynyl, aryl, or
heteroaryl groups (and combinations thereof). Preferably R
represents a relatively bulky group containing at least 4
carbon atoms, and preferably between 4 to 18 carbon atoms.

10

The organophosphoric acid is most preferably di-
2-ethylhexyl phosphoric acid (D2EHPA), however it will be
appreciated by persons skilled in the art that an
organophosphoric acid having extraction characteristics

15   similar to D2EHPA could be used. Organophosphoric acids
have the formula $(RO)_2PO_2H$, in which R represents an
organic group. The two organic groups R, which may be the
same or different, can be selected from optionally
substituted branched, straight chained or cyclic alkyl,

20   alkenyl or alkynyl groups. Preferably the organic groups
are fairly bulky, and have a minimum of 4 carbon atoms,
more preferably from 6 to 18 carbon atoms. The organic
groups may suitably be n-octyl, cyclooctyl or 2-ethylhexyl.

25   In the most preferred embodiment of the
invention, the organophosphinic acid is di-2,4,4-
trimethylpentyl phosphinic acid (eg Cyanex 272). However
it will it will be appreciated by persons skilled in the
art that any organophosphinic acid having extraction

30   characteristics similar to di-2,4,4-trimethylpentyl
phosphinic acid could be used. Organophosphinic acids have
the formula R_2PO_2H, in which R represents an organic group.
The two organic groups R, which may be the same or
different, can be selected from optionally substituted

35   branched, straight chained or cyclic alkyl, alkenyl or
alkynyl groups. Preferably the organic groups are fairly
bulky, and have a minimum of 4 carbon atoms, more

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preferably from 6 to 18 carbon atoms. The organic groups
are preferably unsubstituted branched, straight chained or
cyclic alkyl groups, and may suitably be n-octyl,
cyclooctyl, 2-ethylhexyl or 2,4,4-trimethylpentyl.

5

        The term "alkyl" used either alone or in a
compound word such as "optionally substituted alkyl" or
"optionally substituted cycloalkyl" denotes straight chain,
branched or mono- or poly- cyclic alkyl, preferably C1-30
10   alkyl or cycloalkyl. Examples of straight chain and
branched alkyl include methyl, ethyl, propyl, isopropyl,
butyl, isbutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-
amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-
methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-
15   methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-
dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-
trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-
methylhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-
dimethylpentyl, 4,4-dimetylpentyl, 1,2-dimethylpentyl, 1,3-
20   dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl,
1,1,2-trimethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-
methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-2- or 3-
propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-
methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3-
25   or 4-propylheptyl, undecyl 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-
or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl,
1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl,
1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-
or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-
30   ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3-
or 4-butyloctyl, 1-2-pentylheptyl and the like. Examples
of cyclic alkyl include cyclopropyl, cyclobutyl,
cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl,
cyclononyl and cyclodecyl and the like. The alkyl may
35   optionally be substituted by any non-deleterious
substituent.

In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio and the like.

Suitable optional substituents will be chosen on the basis that the organophosphinic or organophosphoric acid have the desired extraction characteristics, and the substituents do not react with any other component of the mixture under the given extraction conditions.

The term "halogen" denotes fluorine, chlorine, bromine or iodine.

A range of different compounds may be used as the synergist, such as pyridine carboxylate esters, phosphine oxides or oximes (particularly non-chelating oximes). However the synergist is preferably a pyridine carboxylate ester.

The term "pyridine carboxylate ester" is used this specification in its broadest sense to refer to any organic compound containing at least one pyridine group and at least one carboxylate group. Accordingly, the term encompasses 2-pyridine carboxylates, 3-pyridine carboxylates, 4-pyridine carboxylates, and dicarboxylates

of pyridine such as 3,5-pyridine dicarboxylates. The ester
groups may be based on optionally substituted aliphatic
hydrocarbon groups including branched, straight chained or
cyclic alkyl, alkenyl and alkynyl groups. Preferably the

5   aliphatic hydrocarbon groups have between 4 and 18 carbon
atoms, and therefore include n-octyl, 2-ethylhexyl and
cyclooctyl groups.

The term "oxime" is used in this specification in

10   its broadest sense to refer to any organic compound
containing a carbon to nitrogen double bond, with the
nitrogen atom being attached to an oxygen atom.
Accordingly, the term oxime includes within its scope
oximes with a hydroxy group attached to the nitrogen atom,

15   and oxime ethers.

The organic phase for the organophosphoric acid
extraction step includes a modifier in addition to an
organophosphoric acid. The organic phase for the

20   organophosphinic acid extraction step similarly includes a
modifier in addition to an organophosphoric acid.

The modifier is any suitable modifier that
improves separation of the organic and aqueous phases.

25   Suitable modifiers include 2-ethylhexanol, isodecanol and
isotridecanol and tri n-butyl phosphate (TBP). TBP is the
preferred modifier.

The organic solvent may be any suitable organic

30   solvent for the organophosphoric acid that achieves good
phase separation from the aqueous phase with the modifier.
In some respects the organic solvent could be considered to
be a diluent for the extraction agent. Kerosene is the
most common solvent/diluent used for this purpose due to

35   its low cost and availability.

The loaded organic phase resulting from solvent

extraction with organophosphoric acid may be scrubbed with
an aqueous scrub solution containing manganese and copper.
This aqueous scrub solution is preferably obtained by
conducting a selective strip on a scrubbed loaded organic

5   solution produced in the scrubbing step, and recycling the
manganese and copper containing aqueous solution back to
the scrubbing stage to be used as the aqueous scrub
solution. A spent aqueous scrub solution generated in the
scrubbing step is then recycled to the leach solution to

10   maximise the recovery of cobalt (and nickel if present at
that stage of the process). The selectively stripped
organic solution would usually then be subjected to bulk
stripping to remove a large proportion of the cations
remaining therein to be recycled for use as the organic

15   phase in the initial extraction step.

       The scrubbed organic solution may be selectively
stripped of manganese and copper by contacting it with an
acid. Sulphuric acid is preferred due to its low cost,

20   however other acids such as HCl and HNO$_3$ could be used.
The bulk stripping can be conducted by contacting the
selectively stripped organic solution with a second acid.
The second acid needs to be stronger than the first.
Accordingly, when sulphuric acid is used as the first acid,

25   more concentrated sulphuric acid or hydrochloric acid may
be used as the second acid to bulk strip the selectively
stripped organic solution of the impurity elements. The
bulk stripped organic solution may then be recycled for use
as the organic phase in the initial extraction step.

30

       The range of the Mn and Cu in the aqueous scrub
-solution will depend on how much Co (and Ni) is to be
scrubbed and the aqueous to organic (A/O) ratio.
Preferably, the mole ratio of (Mn+Cu)/(Co+Ni) is at least

35   1.5 for complete scrubbing.

       The amount of organophosphoric acid in the

organic solution used in the organophosphoric acid
extraction step will depend on the concentration of the
elements to be extracted and the A/O ratio, however the
amount would typically be in the range of from 3% to 35%
5   v/v, with a preferred range of 5% to 25%. At levels above
35% the organic solution will be too viscous resulting in
lower extraction kinetics.

        The amount of modifier in the organic solution
10   used in the organophosphoric acid extraction step will also
vary. The range of modifier will typically be in the range
of 3% to 15% v/v, with a preferred range of 5% to 10%.

        Preferably, the pH of the aqueous phase is
15   maintained in a range from 3.0 to 4.5 and more preferably
3.5 to 4.0 in the organophosphoric acid extraction. The
temperature is preferably maintained in the range of from
10°C to 60°C, more preferably from 20 to 40°C. Whilst
temperatures as low as 10°C are achievable, a temperature
20   lower than 15°C results in high viscosity. At temperatures
higher than 60°C there is a risk of evaporation and
degradation of the organic phase.

        The aqueous to organic ratio (A/O) in the
25   extraction stage of the organophosphoric acid extraction
step is most preferably 1:1, but may lie in the range from
10:1 to 1:10, and preferably 1:2 to 5:1. The aqueous to
organic ratio maintained in the scrubbing stage of this
step may lie within the range of from 1:5 to 1:200, but
30   preferably it is in the range of 1:5 to 1:20, and most
suitably it is from 1:5 to 1:10.

        The amount of organophosphinic acid in the
organic solution used in the organophosphinic acid solvent
35   extraction step will depend on the concentration of the
elements to be extracted and the A/O ratio, however the
amount would typically be in the range of from 3% to 35%

v/v, with a preferred range of 5% to 25%. At levels above
35% the organic solution will be too viscous resulting in
lower extraction kinetics.

5   Preferably, the pH of the aqueous phase is
maintained in a range from 5.0 to 6.0 in the
organophosphinic acid solvent extraction circuit. The
temperature is preferably maintained in the range of from
10°C to 60°C, more preferably from 20 to 40°C. Whilst
10   temperatures as low as 10°C are achievable, a temperature
lower than 15°C results in high viscosity. At temperatures
higher than 60°C there is a risk of evaporation and
degradation of the organic phase.

15   The aqueous to organic ratio (A/O) in the
organophosphinic acid solvent extraction circuit is most
preferably 1:1, but may lie in the range from 3:1 to 1:3.

          The cobalt extracted into the loaded organic
20   phase in the organophosphinic acid extraction circuit is
stripped therefrom in a stripping stage. In the stripping
stage, the A/O ratio may be from 1:2 up to 1:200, and the
pH from 2.0 to 4.0. Other details concerning the
organophosphinic acid extraction stage are well within the
25   knowledge and experience of persons in the art of the
invention.

          The steps outlined above can be conducted in
combination with other solvent extraction steps and
30   optionally one or more precipitation steps to separate
certain elements from each other. For instance, it is
common in the art of the invention for a preliminary iron
precipitation step to be conducted to precipitate out iron
to leave an aqueous leach solution containing the target
35   elements. However, it is a major advantage of the process
of the present invention that precipitation steps involving
precipitation out of the target elements (such as cobalt

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and nickel) and re-leaching of the precipitate can be
avoided. Even when such a precipitation step is required,
it is to be noted that no precipitation steps for the
purpose of separating manganese from cobalt are required.
5 Therefore, in a preferred embodiment of the invention the
process does not include a sulphide precipitation stage for
separating cobalt from manganese. In a more preferred
embodiment of the invention, the process does not include a
precipitation step involving precipitation out of the
10 target elements and re-leaching of the precipitate.

It will be well understood to persons skilled in
the art of the invention that scrubbing stages of the type
well known in the art may be used for recovering elements
15 even if the scrubbing stages are not specifically
mentioned. The design of the optimum arrangement of
scrubbing stages will depend on the specific aqueous leach
solution and the elements desired to be recovered therefrom
(and target percentage recovery levels).
20

According to the present invention there is also ·
provided a plant for conducting the method described above,
the plant including, in any order:
- a carboxylic acid solvent extraction circuit including a
25   carboxylic acid solvent extractor and a carboxylic acid
       stripper;
- an organophosphoric acid solvent extraction circuit
   including an organophosphoric acid solvent extractor and
   an organophosphoric acid stripper; and
30 - an organophosphinic acid solvent extraction circuit
    including an organophosphinic acid solvent extractor and
    an organophosphinic acid stripper.

Preferably the organophosphoric acid extraction
35 circuit includes:
- a scrubber for scrubbing the loaded organic solution
   generated in solvent extractor;

    - a selective stripper in which the scrubbed organic
solution generated in the scrubber is subjected to
selective stripping to generate the aqueous scrub
solution for use in the scrubber;

5   - a scrubbed organic solution conduit for conducting the
scrubbed organic solution to the selective stripper;

    - an aqueous scrub solution conduit for conducting the
aqueous scrub solution from the selective stripper to
the scrubber; and

10   - a spent aqueous scrub solution conduit for conducting
the spent aqueous scrub solution from the scrubber to
the organophosphoric acid solvent extractor.

        Preferably the plant further includes an organic
15 solution recycle conduit for conducting the partially
stripped scrubbed solution from the stripper to the
organophosphoric acid solvent extractor. More preferably,
a bulk stripper is located in this recycle conduit, in
which the partially stripped scrubbed solution is stripped
20 of remaining impurities before being conducted to the
solvent extractor.

        As will be understood to persons skilled in the
art of the invention, the various solvent extractors are
25 preferably countercurrent solvent extractors. In addition,
further scrubbing stages and vessels or tanks may be
included in the plant.

        The plants described above will also include the
30 necessary conduits for passing the subject streams from one
vessel, stage or circuit to the next. The plants will also
usually include a cobalt recovery stage and a nickel
recovery stage. The cobalt recovery stage may include a
cobalt precipitation vessel or an electrolytic cell in
35 which a cobalt electrowinning process can be conducted.
The nickel recovery stage may include a nickel electrolytic
cell in which a nickel electrowinning process can be

conducted. The arrangement of an appropriate plant
including all of these elements is well within the skill of
a person in the art of the invention now that the direction
has been provided to conduct the process for recovering
5   cobalt in the manner described above.

Some preferred embodiments of the invention are
described in the accompanying examples and figures, in
which:
10   Figure 1 illustrates a flow chart for the one stage in
            the processes of the preferred embodiments of the
            invention as represented in Figures 2 and 4-5, and
            represents schematically a part of the plants of those
            preferred embodiments of the invention;
15   Figure 2 illustrates a schematic flow chart for one
            embodiment of the process of the invention, and
            represents schematically a plant for this embodiment
            of the invention;
            Figure 3 illustrates a schematic flow chart for a
20   second embodiment of the process of the invention (in
            which the organophosphoric acid extraction circuit is
            not used), and represents schematically a plant for
            this embodiment of the invention;
            Figures 4 and 5 illustrate a schematic flow chart for
25   third and fourth embodiments of the process of the
            invention, and represent schematically plants for
            these embodiments of the invention.

In the embodiments of the preferred embodiments
30   of the invention, Versatic (2-hexyl 2-methyl octacarboxylic
acid) is used as the octacarboxylic acid (in kerosene
organic solvent), Cyanex 272 (di-2,4,4-trimethylpentyl
phosphinic acid) is used as the organophosphinic acid, and
D2EHPA (di-2-ethylhexyl phosphoric acid)is used as the
35   organophosphoric acid.

Flow sheets for four alternative embodiments of

the invention are illustrated in Figures 2 to 5. In the
embodiments represented in Figures 2 and 4 to 5, the boxes
referring to "D2EHPA SX" (di-2-ethylhexyl phosphoric acid
solvent extraction) in combination with the boxes "D2EHPA
5   ST" (ST = strip) should be understood to be a short-hand
reference to all of the steps outlined in Figure 1.

The organophosphoric acid extraction stage, which
is a feature of the processes of the first, third and
10 fourth preferred embodiments of the invention, is described
in detail in Figure 1. An aqueous leach solution 1 (which
may be the PLS - plant leach solution - in Figure 2, the
strip liquor from the Versatic strip in Figure 4, or the
strip liquor from the Cyanex strip in Figure 5) is fed into
15 a countercurrent solvent extractor 2 in which the aqueous
leach solution 1 is contacted with an organic extractant
solution 3 comprising a solution of an organophosphoric
acid (D2EHPA) and a modifier (TBP) in an organic solvent
(kerosene). The aqueous raffinate 4 from the solvent
20 extraction contains most of the cobalt (and nickel, if
present in the aqueous leach solution 1) and, to the extent
that it is present, a large proportion of the magnesium,
from which the cobalt (and nickel) may be recovered.

25 The loaded organic liquor 5 from the solvent
extractor 2 is scrubbed in a scrubber 6 with a scrub
solution 7 containing manganese and copper. Scrubbed
loaded organic solution 8 is selectively stripped with a
first acid, a dilute sulphuric acid 9, in a stripper 10 to
30 form scrub solution 7, part of which is recycled to
scrubber 6. Partially stripped organic extractant 11 is
then stripped of all impurities with a second acid, dilute
hydrochloric acid 12, in a bulk stripper 13. Stripped
organic solution 3 is recycled to extractor 2.
35

Figure 2 is a flow chart illustrating a process
which combines an initial solvent extraction process using

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di-2-ethylhexyl phosphoric acid (D2EHPA) with two further
solvent extraction processes using 2-hexyl, 2-methyl
octacarboxylic acid (Versatic 10) and an organophosphinic
acid respectively, to recover nickel and cobalt.

5

Figure 3 is a flow chart illustrating a process
which combines a synergistic SX process using 2-hexyl, 2-
methyl octacarboxylic acid (Versatic 10) as extractant and
a synergist, with a further SX process using an
organophosphinic acid, to recover nickel and cobalt.

10

Figures 4 and 5 illustrate a process which
combines a synergistic SX process using 2-hexyl, 2-methyl
octacarboxylic acid (Versatic 10) as extractant and a
synergist, with two further SX processes using di-2-
ethylhexyl phosphoric acid (D2EHPA) and an organophosphinic
acid respectively, to recover nickel and cobalt. This
process is more robust than the process described with
reference to Figure 3.

15

20

Figure 4 shows a flow chart in which 2-hexyl, 2-
methyl octacarboxylic acid (Versatic 10) and a synergist
such as pyridine carboxylate ester (Acorga CLX50 - a
commercially available pyridine carboxylate diester) are
used in the first solvent extraction stage, di-2-ethylhexyl
phosphoric acid (D2EHPA) is used in the second solvent
extraction stage and the organophosphinic acid di-2,4,4-
trimethylpentyl phosphinic acid (Cyanex 272) is used in the
third solvent extraction stage. Figure 5 shows the
situation when the latter two SX stages are reversed such
that 2-hexyl, 2-methyl octacarboxylic acid (Versatic 10)
and a synergist such as pyridine carboxylate ester (Acorga
CLX50) are used in the first solvent extraction stage, the
organophosphinic acid acid di-2,4,4-trimethylpentyl
phosphinic acid (Cyanex 272) is used in the second solvent
extraction stage and di-2-ethylhexyl phosphoric acid
(D2EHPA) is used in the third solvent extraction stage.

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More specifically, as shown in Figure 1,

(a) Zinc, calcium, copper and manganese are separated from nickel, cobalt and magnesium using D2EHPA. The loaded organic phase resulting from solvent extraction with D2EHPA may be scrubbed with an aqueous solution containing manganese and copper. The aqueous scrub solution may then be recycled to the leach solution to maximise the recovery of cobalt and nickel (Fig 1).

(b) Versatic 10 is used to separate nickel and cobalt from magnesium. Nickel and cobalt are concentrated by stripping at a high organic/aqueous (O/A) flowrate ratio (Fig. 2)

(c) An organophosphinic acid is used to separate cobalt from nickel. Cobalt is further concentrated by stripping at a high O/A flow rate ratio,

(d) Both nickel and cobalt could be recovered by electrowinning, precipitation or any other appropriate method.

In a less-favoured variation of this process, the order of the Versatic 10 and organophosphic acid SX processes could be reversed, however this would result in the cobalt only being concentrated through one extraction/stripping cycle making its recovery (by electrowinning or precipitation or any other appropriate process) less favourable.

More specifically in Figure 3,

(a) Nickel, cobalt, zinc and copper are separated from calcium, magnesium and manganese by synergistic solvent extraction using Versatic 10 and a synergist. Scrubbing will be required for complete separation of the cobalt and manganese.

(b) Nickel, cobalt and zinc are concentrated by stripping the loaded organic solution with a high O/A flowrate ratio in the first stripping stage,

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(c) Copper is then stripped in a second stage with stronger acid and separated as a by-product,

(d) Zinc and cobalt are separated from nickel by solvent extraction using an organophosphinic acid,

5 (e) Cobalt is concentrated by stripping the loaded organic solution with a high O/A flowrate ratio in the first stripping stage,

(f) Zinc is then stripped in a second stage with stronger acid and separated as a by-product,

10 (g) Nickel and cobalt can be recovered by either electrowinning, precipitation or any other appropriate process

More specifically in Figure 4,

15 (a) Nickel, cobalt, zinc and copper are separated from calcium, magnesium and manganese by synergistic solvent extraction using Versatic 10 and a synergist. Scrubbing may not be required for complete separation of the cobalt and manganese as manganese can be
20 separated in the next SX process step. The synergist is necessary to effect complete separation of the Ca (to the raffinate) during extraction and thereby prevent gypsum precipitation during stripping. If the leach solution entering solvent extraction has only a
25 low calcium concentration, use of the synergist may not be necessary as calcium can also be separated in the next SX process step.

(b) Nickel, cobalt and zinc (and any remaining manganese) are concentrated by stripping the loaded organic
30 solution with a high O/A flowrate ratio in the first stripping stage,

(c) Copper is then stripped with stronger acid and separated as a by-product (alternatively, a bulk strip can be used, in which case copper will also be
35 concentrated with the nickel cobalt and zinc),

(d) Zinc (and any remaining copper, manganese and calcium) are separated from the nickel and cobalt using D2EHPA,

(e) Cobalt is separated from nickel by solvent extraction
     using an organophosphic acid,

(f) Cobalt is concentrated by stripping the loaded organic
     solution with a high O/A flowrate ratio,

5 (g) Nickel and cobalt can be recovered by either
        electrowinning, precipitation or any other appropriate
        process.

In a variation of this process, the order of the
10 D2EHPA and organophosphic acid SX processes could be
reversed (Fig 5). Figure 5 shows cobalt being recovered by
precipitation. Alternatively, cobalt could be electrowon
with the spent electrolyte being returned to the
organophosphic acid strip circuit.

15

A synergist is used with Versatic 10 in processes
2 and 3 to help separate manganese and calcium from nickel
and cobalt. The synergistic effect is to move the nickel
and cobalt isotherms to lower pH values, thereby increasing
20 the pH gap (ΔpH$_{50}$) to the manganese and calcium isotherms
and thus promoting better separation. Pyridine-based
synergists such as pyridine carboxylate ester (Acorga
CLX50) have proved suitable for this purpose. Other
synergists demonstrating a similar effect may be used.

25

The preferred embodiments described above will
now be described in further detail with reference to the
accompanying examples.

30 EXAMPLE 1 (Fig 4)
Synergistic solvent extraction with Versatic 10 and CLX50.
The aim of synergistic solvent extraction with
Versatic 10 and CLX50 is to promote separation of nickel
and cobalt from manganese and calcium by increasing the pH
35 gap, ΔpH$_{50}$, between their respective isotherms. Copper and
zinc extract with the nickel and cobalt; magnesium reports
to the raffinate with the manganese and calcium

pH isotherms and distribution isotherms were
determined with Versatic 10 and CLX50. The pH isotherms of
nickel and cobalt with Versatic 10 were significantly
5   affected by the addition of CLX50. As a result, the
addition of CLX50 as a synergist substantially enlarged the
pH_{50} difference between cobalt and manganese pH isotherms.
The ΔpH_{50} between manganese and cobalt increased from 0.28
pH units without CLX50 to 0.85 pH units with 20% CLX50 as
10   synergist. The ΔpH_{50} between calcium and nickel increased
from 0.77 pH units without CLX50 to 1.87 pH units with 20%
CLX50 as synergist. Shellsol 2046 was used as diluent in
these experiments.

15   EXAMPLE 2 (Figs 1, 4 and 5)
Separation of nickel and cobalt from manganese and other
impurities, using a synthetic nickel laterite acid leach
solution.

20   1. Extraction with D2EHPA
The aim of the extraction with D2EHPA is to
extract all the zinc, calcium, copper and manganese from
the aqueous leach solution (PLS) into the organic D2EHPA
solution and to minimise the extraction of cobalt, nickel
25   and magnesium.

The aqueous solution was a synthetic iron-free
laterite leach solution containing 2.60 g/L Ni, 0.24 g/L
Co, 0.27 g/L Zn, 0.52 g/L Ca, 0.09 g/L Cu, 1.87 g/L Mn and
30   2.89 g/L Mg. The organic solution consisted of 12% di-2-
ethylhexyl phosphoric acid (D2EHPA), 2.5% tri-n-butyl
phosphate (TBP) and 85.5% kerosene (Shellsol 2046), all by
volume. Four counter-current extraction stages were used at
an A/O flowrate ratio of 1:1. The pH in the four mixers was
35   controlled at 3.7 using three pH controllers with the
addition of ammonia solution (Fig 1). The results are shown
in Table 1. All the zinc, calcium, manganese and copper

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were extracted in four stages. Some 12.6% of the cobalt,
20% of the magnesium and no nickel were co-extracted. The
raffinate contained only cobalt, nickel and magnesium.

5   If the D2EHPA extraction described above had been
preceded by synergistic SX with Versatic 10 and CLX50, Mg
and Ca would already have been removed (Figs 3 and 4),
leaving only Co and Ni in the D2EHPA raffinate (Fig 4).
The Ni/Co raffinate could then proceed to a subsequent
10 solvent extraction step where cobalt would be extracted
from the aqueous solution by di-2, 4, 4-trimethylpentyl
phosphinic acid (Cyanex 272), using a well proven
commercial process. The cobalt and nickel could be then
recovered by electrowinning from the Cyanex strip and
15 raffinate solutions respectively (Fig 4).

           Alternatively, if the D2EHPA extraction described
above had been preceded by both synergistic SX with
Versatic 10 and CLX50 and a known Cyanex 272 extraction,
20 Ni, Mg and Ca would already have been removed, leaving only
Co in the D2EHPA raffinate, which could be recovered by
hydroxide precipitation (Fig 5), or by electrowinning with
the cobalt electrowinning spent electrolyte containing
sulphuric acid being recycled to the Cyanex strip. Ni
25 could be recovered by electrowinning from the Cyanex
raffinate.

           In both flowsheet configurations (Figs 4 and 5),
the nickel electrowinning spent electrolyte containing
30 sulfuric acid would be recycled to the Versatic 10 strip.

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Table 1   Summary of semi-continuous extraction test results

Metal name	Concentration (g/L)			Total extraction (%)
	In feed	In loaded organic	In raffinate	
Zn	0.265	0.255	0.000	100.00
Ca	0.516	0.605	0.000	100.00
Mn	1.865	1.775	0.000	100.00
Cu	0.094	0.089	0.000	100.00
Co	0.240	0.031	0.196	12.57
Ni	2.597	0.000	2.535	0.000
Mg	2.893	0.590	2.130	20.12

2. Scrubbing the D2EHPA organic (Fig 1)

The aim of scrubbing is to scrub any cobalt and nickel that is inevitably co-extracted with zinc, calcium, copper and manganese, from the D2EHPA organic extraction solution to the aqueous scrub raffinate and to minimise the scrubbing of manganese, copper, calcium and zinc.

Two scrubbing stages were used with a combined solution of manganese (6.78 g/L) and copper (0.35 g/L) at an A/O flowrate ratio of 1:5. Scrubbing results are listed in Table 2. The cobalt and nickel scrubbing efficiencies were 100% with no cobalt and nickel being left in the organic solution. This scrub raffinate containing 0.142 g/L cobalt would be recycled back to the D2EHPA extraction feed. By doing this, the cobalt and nickel recovery would approach 100%.

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Table 2 Summary of scrubbing test results using a combined
Mn and Cu scrub solution

Metal name	Concentration (g/L)				Total scrub efficiency (%)
	Scrub solution	loaded organic	scrubbed organic	scrub raffinate	
Zn	0.000	0.255	0.256	0.000	0.00
Ca	0.035	0.605	0.610	0.054	-0.82
Mn	6.781	1.775	3.095	0.926	-41.65
Cu	0.349	0.089	0.146	0.112	-35.45
Co	0.000	0.031	0.000	0.142	100.00
Ni	0.000	0.000	0.000	0.001	100.00
Mg	0.019	0.590	0.000	2.372	100.00

3. Selective stripping of D2EHPA organic (Fig 1)
        The aim of selective stripping is to generate a
solution containing mainly manganese and copper for using
as scrubbing solution in the previous stage.

        One selective strip stage was used at an A/O
flowrate ratio of 1:5 with 14.9 g/L sulphuric acid. The
results are shown in Table 3. The strip raffinate contained
7.3 g/L manganese and 0.54 g/L copper, which was just
slightly higher than the scrubbing solution used in the
previous stage (6.78 g/L manganese and 0.35 g/L copper).
However this could be easily corrected by using slightly
more dilute sulphuric acid for stripping, say 12 g/L.

4. Bulk stripping of D2EHPA organic (Fig 1)
        The aim of bulk stripping is to re-generate the
organic D2EHPA solution by stripping all elements from the
organic extractant.

        Two bulk strip stages were used at an A/O

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flowrate ratio of 1:5 with 37 g/L hydrochloric acid. The
results are also shown in Table 3. All the zinc, calcium,
copper and manganese were stripped. If no calcium is
present in the feed, sulphuric acid can be used for bulk
5   stripping.

Table 3   Summary of semi-continuous stripping test results
10   with an A/O ratio of 1:5

Metal name	Concentration (g/L)			Total strip efficiency (%)
	Scrubbed organic	Stripped organic 1	Strip raffinate 1	
(Selective strip, 14.9 g/L H$_2$SO$_4$)				
Zn	0.256	0.255	0.022	1.73
Ca	0.610	0405	0.280	33.28
Mn	3.095	1.570	7.319	46.78
Cu	0.146	0.030	0.540	78.26
(Bulk strip, 36.6 g/L HCl)				
	Stripped organic 1	Stripped organic 2	Strip raffinate 2	
Zn	0.255	0.000	1.494	100.00
Ca	0.405	0.000	2.401	100.00
Mn	1.570	0.000	8.679	100.00
Cu	0.030	0.000	0.159	100.00

It will be understood to persons skilled in the
art of the invention that various modifications could be
15   made to the preferred embodiments illustrated and described
above without departing from the spirit and scope of the
invention.

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CLAIMS:

1.   A method of separating nickel, cobalt or both
from other cations contained in a leach solution, the
method including the steps of subjecting the leach solution
to separate solvent extraction steps using an
organophosphoric acid, a carboxylic acid and an
organophosphinic acid.

2.   The method as claimed in claim 1, wherein the
carboxylic acid extraction step is conducted with a mixture
of carboxylic acid and a synergist that is capable of
increasing the pH gap, ΔpH_{50}, between isotherms for nickel
and cobalt and those for manganese and calcium, wherein the
pH_{50} value is the pH at which 50% metal extraction is
achieved.

3.   The method as claimed in claim 2, wherein the
synergist is selected from the group consisting of pyridine
carboxylate esters, phosphine oxides and oximes.

4.   The method as claimed in any one of the preceding
claims, wherein the carboxylic acids is the formula RCOOH,
in which R represents any optionally substituted aliphatic
or aromatic group, or a combination of these groups.

5.   The method as claimed in claim 4, wherein R
contains at least 4 carbon atoms.

6.   The method as claimed in claim 4, wherein R
contains between 4 and 18 carbon atoms.

7.   The method as claimed in any one of the preceding
claims, wherein the carboxylic acid is 2-hexyl, 2-methyl
octacarboxylic acid or a carboxylic acid having extraction
characteristics similar to or the same as 2-hexyl, 2-methyl
octacarboxylic acid.

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8.   The method as claimed in any one of the preceding claims, wherein the organophosphoric acid is of the formula $(RO)_2PO_2H$, in which each R group, which may be the same or different, is an optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl group.

9.   The method as claimed in claim 8, wherein each R group has a minimum of 4 carbon atoms.

10.   The method as claimed in claim 8, wherein each R group has between 6 to 18 carbon atoms.

11.   The method as claimed in claim 8, wherein R is n-octyl, cyclooctyl or 2-ethylhexyl.

12.   The method as claimed in any one of claims 1 to 7, wherein the organophosphoric acid is di-2-ethylhexyl phosphoric acid, or an organophosphoric acid having extraction characteristics similar to or the same as di-2-ethylhexyl phosphoric acid.

13.   The method as claimed in any one of the preceding claims, wherein the organophosphinic acid is of the formula R_2PO_2H, in which the two R groups, which may be the same or different, are selected from optionally substituted branched, straight chained or cyclic alkyl, alkenyl or alkynyl groups.

14.   The method as claimed in claim 13, wherein the two R groups each contain a minimum of 4 carbon atoms.

15.   The method as claimed in claim 13, wherein the two R groups each contain from 6 to 18 carbon atoms.

16.   The method as claimed in any one of claims 1 to 12, wherein the organophosphinic acid is di-2,4,4-

trimethylpentyl phosphinic acid or an organophosphinic acid having extraction characteristics similar to or the same as di-2,4,4-trimethylpentyl phosphinic acid.

5   17.   The method as claimed in any one of the preceding claims, wherein a modifier is used in the organophosphoric and organophosphinic acid solvent extraction stages to facilitate phase separation of the aqueous and organic phases.

10

18.   The method as claimed in claim 17, wherein the modifier is tri n-butyl phosphate.

19.   The method as claimed in any one of the preceding
15   claims, wherein the organic solvent used in the carboxylic acid, organophosphoric acid and organophosphinic acid solvent extraction stages is kerosene.

20.   The method as claimed in any one of the preceding
20   claims, wherein the loaded organic phase resulting from solvent extraction with organophosphoric acid is scrubbed with an aqueous scrub solution containing manganese and copper, which aqueous scrub solution is obtained by conducting a selective strip on a scrubbed loaded organic
25   solution produced in the scrubbing step, and recycling the manganese and copper-containing aqueous solution back to the scrubbing stage to be used as the aqueous scrub solution.

30   21.   The method as claimed in claim 20, wherein a spent aqueous scrub solution generated in the scrubbing step is then recycled to the leach solution of the organophosphoric acid extraction step to maximise the recovery of cobalt (and nickel, if present), and the
35   selectively stripped organic is subjected to bulk stripping to remove a large proportion of the cations remaining therein to be recycled for use as the organic phase for the

organophosphoric solvent extraction..

22.   The method as claimed in claim 20 or claim 21,
wherein the mole ratio of (Mn+Cu)/(Co+Ni) in the aqueous
5   scrub solution is at least 1.5.

23.   The method as claimed in any one of the preceding
claims, wherein the method does not include a sulphide
precipitation stage for separating cobalt from manganese.
10

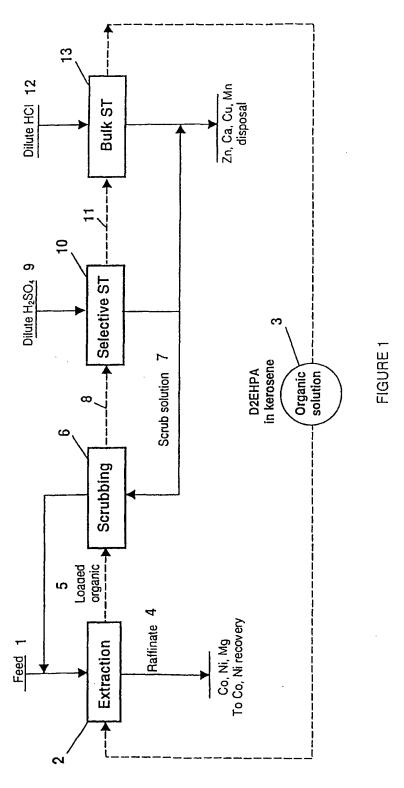24.   A method for separating nickel, cobalt or both
from other cations contained in a leach solution, the
method involving subjecting the leach solution to separate
solvent extraction steps using:
15   (a)   an organophosphinic acid; and
      (b)   a carboxylic acid in combination with a synergist that
            is capable of increasing the pH gap, ΔpH_{50}, between
            isotherms for nickel and cobalt and those for
            manganese and calcium.
20

25.   A plant for conducting the method as claimed in
any one of claims 1 to 23, the plant including, in any
order:
      -   a carboxylic acid solvent extraction circuit including a
25   carboxylic acid solvent extractor and a carboxylic acid
            stripper;
      -   an organophosphoric acid solvent extraction circuit
            including an organophosphoric acid solvent extractor and
            an organophosphoric acid stripper; and
30   -   an organophosphinic acid solvent extraction circuit
            including an organophosphinic acid solvent extractor and
            an organophosphinic acid stripper.

26.   The plant as claimed in claim 25, wherein the
35   organophosphoric acid extraction circuit includes:
      -   a scrubber for scrubbing the loaded organic solution
            generated in solvent extractor;

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    - a selective stripper in which the scrubbed organic solution generated in the scrubber is subjected to selective stripping to generate the aqueous scrub solution for use in the scrubber;

5   - a scrubbed organic solution conduit for conducting the scrubbed organic solution to the selective stripper;

    - an aqueous scrub solution conduit for conducting the aqueous scrub solution from the selective stripper to the scrubber; and

10   - a spent aqueous scrub solution conduit for conducting the spent aqueous scrub solution from the scrubber to the organophosphoric acid solvent extractor.

27.   The plant as claimed in claim 26, wherein the
15 plant further includes an organic solution recycle conduit for conducting the partially stripped scrubbed solution from the stripper to the organophosphoric acid solvent extractor.

20 28.   The plant as claimed in claim 27, wherein a bulk stripper is located in the recycle conduit, in which the partially stripped scrubbed solution is stripped of remaining impurities before being conducted to the solvent extractor.
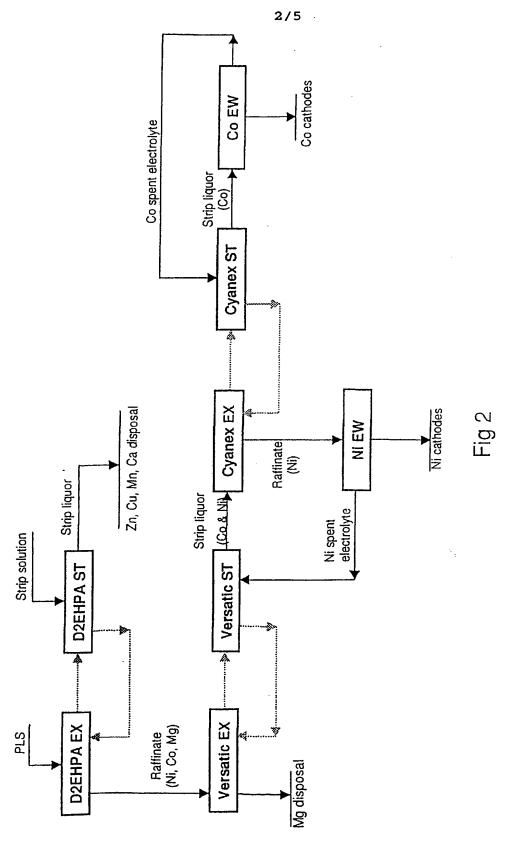25

29.   The plant as claimed in any one of claims 25 to 28, the plant including cobalt and nickel recovery stages for recovering cobalt and nickel.
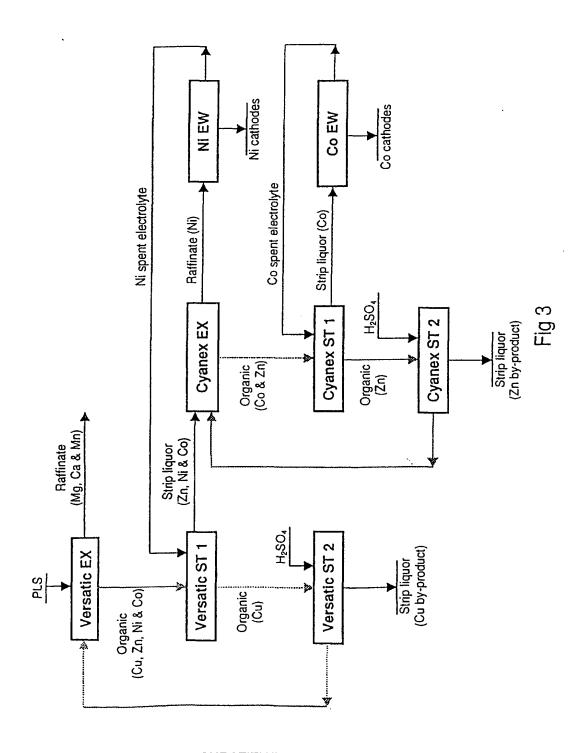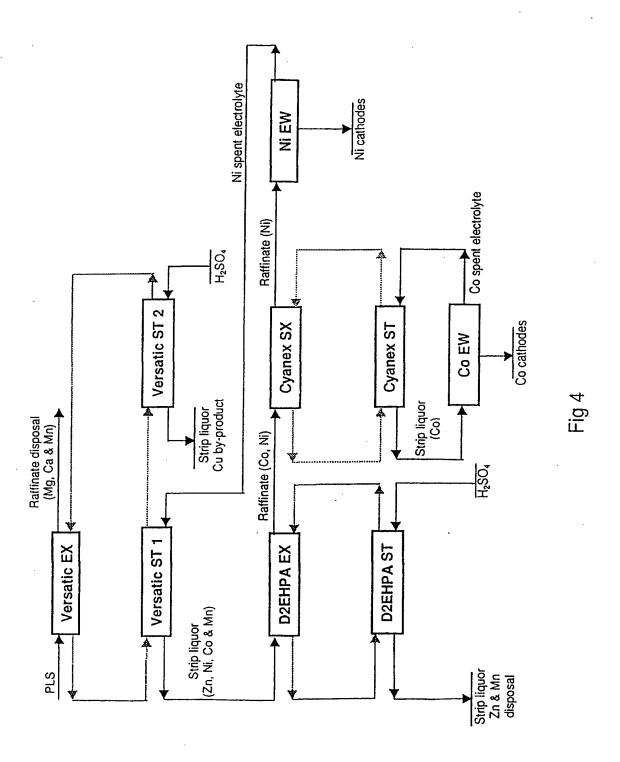
FIGURE 1

Fig 2

Fig 3

Fig 4

5 / 5

Fig 5

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]:   C22B3/26,3/32,3/38,23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22B3/26,3/32,3/38,23/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU IPC AS ABOVE.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT; nickel,cobalt,solvent,extract

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU A 40890/96 (Resolute Resources Ltd.) (18/07/96	
A	EP A 0617135 (Preston ,J.S.) (28/09/94)	

☐ Further documents are listed in the continuation of Box C   ☒ See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 October 2001	3 0 OCT 2001
Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	G.Carter Telephone No : (02) 6283

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
EP	061135	NONE
AU	40890/96	NONE

END OF ANNEX

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